

EVALUATION OF MICROWAVE DIGESTION AS THE PREPARATION METHOD FOR MERCURY-IN-COAL MEASUREMENT

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INTRODUCTION

The 1990 Clean Air Act Amendment (CAAA) empowered the U.S. Environmental Protection Agency (EPA) to set emission standards for a number of potentially hazardous air pollutants (HAPs) generated by a variety of specific combustion sources. Eleven elements (or compounds of these elements) present in coal are among the 189 pollutants identified as air toxics by the CAAA legislation. Mercury is included in this list. Generally mercury concentrations in coal are well below 1 ppm (1 $\mu\text{g/g}$). However, because such a large tonnage of coal is consumed for electric power generation, coal combustion represents a potentially significant source of mercury entering the environment (1).

Determination of the concentration of mercury in coal is becoming an increasingly important issue. Because of the relatively low concentration of mercury in coal and the relatively high detection limits of current analytical methods, information on the mercury content of coals to any degree of certainty is still unavailable. Therefore, evaluating the precision and accuracy of current analytical methods and improving existing methods are very important in estimating potential atmospheric emissions and associated risks.

Complete sample dissolution is necessary prior to instrumental analysis for most solid samples. In general, this step is the most critical in trace metal analysis and is time-consuming and labor-intensive. Several preparation methods are currently being used for mercury-in-coal measurements. A method (2) that combusts the coal sample in a tube furnace and collects the mercury vapor using a gold wire collector has shown some higher results (1) compared to other methods. Method ASTM D3684 uses an applied oxygen combustion bomb on the coal sample and subsequent rinsing of the inside of the bomb after combustion. Method SW846 is an open-beaker acid digestion method, which has been considered not suitable for mercury determination because of the volatile properties of mercury. The method presented here has proven to be reliable and rapid for the decomposition of coal samples for mercury determination, as well as for other trace metals.

EXPERIMENTAL

Instrumentation

A Model MDS-2100 microwave oven (CEM Corporation) with pressure control was used. The power range (maximum 950 W) of the oven was adjusted to 1% increments. Since the sample decomposition consists of several separate stages of control, the microwave is also equipped with a removable 12-position carousel. Teflon vessels of 100-mL volume, allowing a maximum 120 psi of pressure, were used.

A Leeman Labs, Inc., PS200 automated mercury analyzer was used as the analytical instrument to measure the mercury in digested coal acid solutions. The pump rate was 5 mL/min. The gas flow rate was 0.3 L/min.

Reagents and Standards

Concentrated sulfuric acid, concentrated nitric acid, and concentrated hydrochloric acid were all trace metal grade. SnCl_2 and $\text{Mg}(\text{ClO}_4)_2$ were analytical grade. Mercury standards were analytical grade.

Procedures

Microwave Digestion

Approximately 0.5 g of coal, accurately weighed to 0.0001 g, was placed in a Teflon microwave digestion vessel with 1 mL of concentrated sulfuric acid and 0.25 mL of concentrated nitric acid (added separately). Approximately 2 minutes was given for the reaction to take place. An additional 1 mL of concentrated nitric acid was then added to the vessel. The digestion vessels were capped and placed

in the microwave, and Step 1 was run (See Table 1). The vessels were removed from the microwave after the run was completed. The vessels were cooled to room temperature and the gases vented. An additional 2 mL of concentrated nitric acid was added to the vessel. The digestion vessels were put through additional heating (Steps 2 and 3) until the solution was a clear light yellow color, with cooling and venting between each step. 0.5 mL of concentrated hydrochloric acid was put in each digestion vessel, and Step 4 was run. 5 mL of concentrated hydrochloric acid was added, and the solution was diluted to 50.0 mL with distilled water in a volumetric flask. The solution was filtered and run on the cold-vapor atomic adsorbance (CVAA) mercury analyzer using matrix-matched standards.

Cold-Vapor Atomic Absorption Mercury Analyzer

After about 1 hour equilibrating the instrument, a five-point calibration was performed. A quality control standard was analyzed immediately after the instrument was standardized to verify calibration accuracy. Samples were run in duplicate, with the mean reported. A calibration check standard was analyzed every ten samples. If the check standards did not read within 10% of the expected value, the instrument was recalibrated. A sample spike was performed every ten samples as well as for each different matrix to verify analyte recovery. A digestion blank and one standard reference material was run along with the samples for quality assurance.

RESULTS AND DISCUSSION

Effect of Acids in Combination

Hot concentrated perchloric acid is a strong oxidizing agent that attacks metals that are unresponsive to other acids. However, hot concentrated perchloric acid is potentially explosive when in contact with organic material (3). Because of this potential hazard, alternative acids to complete dissolution were investigated, and perchloric acid was not used.

Sulfuric acid is a highly effective solvent for many organic samples. Hot concentrated sulfuric acid can completely destroy almost all organic compounds. In this study, sulfuric acid was added as the first step to convert the organic compounds in the coal to inorganic carbon. Because sulfuric acid absorbs the water generated during the reaction, the equilibrium is pushed to the right, helping to maintain the reaction.

Nitric acid is a strong oxidizing reagent widely used for liberating trace metals from various types of matrices as highly soluble nitrate salts. Nitric acid added after the sulfuric acid will convert inorganic carbon to carbon dioxide and produce soluble salts. But only a small amount (0.25–0.5 mL) of nitric acid should be added at first to allow the reaction to start at ambient temperature. If 3 mL of total nitric acid was added at one time, the reaction between the coal and acids would actually slow down as a result of the large amount of water in the concentrated nitric acid (more than 30%) absorbing the heat.

Hydrochloric acid is used for dissolution of coal and, more importantly, for preserving mercury in solution.

Bloom (4) and other researchers (5) reported that most trace metals, including mercury, are completely leached from silicate and sulfide minerals by hot acids; thus there is no need for complete hydrofluoric acid breakdown. Trials using hydrofluoric acid at the end of the digestion stage were carried out in this investigation. The analysis results showed no difference. Therefore, hydrofluoric acid was not used in the digestions.

A comparison was made of digestions with and without sulfuric acid. The results showed a 50% longer digestion time for complete dissolution without sulfuric acid. Adding a mixture of the acids to the coal sample instead of adding them separately was tested. Longer digestion times and incomplete digestions resulted in poor precision and accuracy.

Efficiency of Digestion

Although many studies have been devoted to evaluate recoveries of trace metals from coal matrices, little has been done to establish how completely the coal was digested. If a clear and colorless solution resulted, it has been assumed that digestion was complete. A visible residue of silicate material (a grayish color) often remained. In the case of high-ash coals, the presence of this residue made confirmation of complete digestion even harder. Matusiewicz et al. (5) used total residual carbon to evaluate the degree of completion of digestion. This digestion method was used in several interlaboratory proficiency studies and round-robin studies for mercury and other trace metals, and the overall results indicate that this digestion method is precise and accurate.

Pressure Evaluation

The pressure of the first stage was set at 40 psi, and the power was set with slow ramp. The running time should be adequate to allow the sulfuric acid to react with the coal completely. The maximum pressure in the second stage was raised to 70 psi, because after additional nitric acid is added, the reaction between inorganic carbon and nitric acid can be very violent and large amounts of gases can be generated, resulting in a rapid pressure increase and membrane blowout. The pressure control was connected to the vessel containing the largest and, presumably, the most reactive sample when different types of samples were digested at the same time. Different types (i.e., different ranks) of coal have different responses to microwave pressure. Low-rank coal tends to be digested fairly easily because of its loose organic structure and low carbon content. High pressure is generated in the first couple of steps as a result of the rapid chemical reaction. A low percentage of microwave power should be applied to such samples.

Potential Sources of Interference and Contamination

Organic matrices cause interference on inorganic instrumentation. Some researchers used postdigestion methods such as a potassium persulfate digestion after the microwave digestion to reduce the organic matrices. But we found the method presented here provides a good, complete digestion with good precision and accuracy without any postdigestion. Also, postdigestion can potentially become a source for contamination.

Matrix-matched standards were used to compensate for any contamination from the trace-metal-grade acids used.

The mineral content in coal gave very small or no interference on instrument readings because of the very small amount of mineral content left after the complete digestion.

A digestion blank is very important for accurate analyses of the trace level of analytes in most fossil fuel samples. As impurities in the acids used are compensated for using matrix-matched standards, the digestion blank will verify other potential sources of contamination occurring during the digestion period.

Precision and Accuracy

Without any other laboratory's involvement for testing the method, we cannot verify this method's precision and accuracy, but we can discuss the data we generated from the perspective of precision and accuracy. Tables 2 and 3 show the instrumental precision and digestion precision and accuracy for the three standard reference materials used in this investigation.

A relatively large sample size, about 0.5 g compared with most other methods using 0.1–0.2 g, gives more analyte in the solution provided, resulting in a more accurate reading, since mercury in most of the coals are at trace levels and are barely above the instrument detection limit after the dissolution.

Instrument Detection Limit

The instrument detection limit for coal matrices was calculated based on the seven readings of several different low-level mercury matrix-matched standard concentrations (between 0.1 and 0.5 ppb). The method used for calculation was Code of Federal Regulations 40. The detection limit for coal on the instrument used in this study is 0.1 $\mu\text{g/L}$ in digestion solution or 0.01 $\mu\text{g/g}$ in solid, based on 0.5 g of coal digested and brought to a final volume of 50 mL.

CONCLUSION

Sample digestion in pressurized Teflon vessels using microwave heating proved to be a very rapid method for the complete digestion of fossil fuel samples. Results obtained from this study for trace mercury in coal are in good agreement with certified values. The use of HClO_4 at high temperature and high pressure should be avoided because of the potentially explosive nature of the acid. Multiple digestions and analysis for other important trace metals in a certified standard reference material (National Institute of Standards and Technology) [NIST] 1635 and South Africa Reference Material [SARM] 19 were carried out by the Analytical Research Laboratory investigators at the Energy & Environmental Research Center. Data showed that this digestion method is a good coal dissolution method for other trace metals (As, Cd, Ni, Se, Cr, Be, etc.) in coal.

REFERENCES

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TABLE 1

The Microwave Setup								
Coal Digestion Step 1					Coal Digestion Step 2			
Stage	1	2	3	4	Stage	1	2	3
Power	25	35	40	40	Power	40	45	50
PSI	30	40	45	50	PSI	30	40	60
Time (min)	10	10	60	60	Time (min)	10	10	30
TAP (min)	1	1	60	60	TAP (min)	1	1	30
Fan	100	100	100	100	Fan	100	100	100

Coal Digestion Step 3				Coal Digestion Step 4			
Stage	1	2	3	Stage	1	2	3
Power	30	50	60	Power	35	50	60
PSI	60	85	100	PSI	80	90	100
Time (min)	10	10	20	Time (min)	10	10	20
TAP (min)	1	1	20	TAP (min)	1	1	20
Fan	100	100	100	Fan	100	100	100

TABLE 2

Instrumental Precision			
	1635	SARM 19	SARM 18
% RSD *	2.40	2.45	2.43

* % relative standard deviation (RSD) was from seven readings.

TABLE 3

Digestion Precision and Accuracy						
	SARM	NIST	SARM 18	Commanche	Absaloka	Blacksville
Uncertified Value	0.2	0.02	0.04	NA*	NA	NA
EERC Result	0.207	0.0186	0.024	0.071	0.049	0.084
% RSD**	11.9	32.8	2.56	8.2	19.0	23.9
Number of Digestions	14	12	8	NA	NA	NA
% Recovery	104	93	60	NA	NA	NA

* Not applicable.

** % RSD was calculated from number of digestions.